KINETIC STUDIES ON THE CATALYTIC DECOMPOSITION OF AMMONIUM PERCHLORATE

By

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The available data on the effect of different oxides and salts on the slow and fast decomposition and ignition of ammonium perchlorate are reviewed. On the basis of the effeciency of the additives the most important properties of the catalysts, playing an essential part in accelerating the decomposition of ammonium perchlorate, are pointed out.

Introduction

In an earlier publication [1] we summarized the main results of studies relating to the slow and fast decompositions, the sublimation and the explosion of pure ammonium perchlorate (AP). It is a characteristic feature of AP that its stability is extremely sensitive to the presence of various additives. Depending on their structures and chemical properties, these additives increase the rate of the slow decomposition of AP, decrease the ignition temperature and also affect the rate of combustion of AP. Considering that AP plays a key-role in solid propellants, it can be seen that from the point of view of the increase in performance of the propellant the discovery of the most suitable catalysts is of fundamental importance. Research work in this field began about 10—12 years ago, primarily in laboratories dealing with the production and development of propellants.

However, the considerable sensitivity of the stability of AP to the presence of foreign substances also aroused interest, since this property provided the possibility for the elucidation of the regularities of solid-phase catalytic processes, an area of catalytic reactions which had been completely neglected up to that time.

The present paper summarizes the main results of studies made in this field and the reaction mechanisms proposed by different authors. The effects of various salts and oxides are surveyed separately, greater stress being placed on the kinetic studies. Since, in several cases, the effect of a given substance has been examined by a number of research groups, the characteristics of the effects of additives are always reported on the basis of the first detailed kinetic study. Only the more important results and observations of other work are emphasized.

In addition to the studies published in the various technical journals, numerous special publications, research institute reports and proceedings also deal with the catalytic decomposition of AP. It was possible to obtain some of these, while knowl-

edge about others can be extracted from earlier reviews. It is clear that the greater part of the data published elsewhere than in international journals is of a fairly qualitative nature, and the restricted publication can in many respects be attributed to this and not to the special nature of the subject.

Kinetic studies

Effect of oxides on the decomposition of AP

Manganese dioxide

It was first observed by BIRCUMSHAW and NEWMAN [2] that MnO_2 exerts a very great effect on the decomposition of AP at 235 °C.

The first detailed kinetic measurement series with MnO_2 was made by GALWEY and JACOBS [3] in the range 137—212 °C. The reaction proceeded in two steps. The first stage, which had the higher rate, was a manganese dioxide catalysed process, while the second corresponded to the decomposition of pure AP.

For MnO_2 contents of 34—90% the rate constant of the catalysed reaction was independent of the composition of the sample. This result indicates that the rate of the catalytic reaction depends primarily on the extent of the contact surface between the oxide and the AP and not on the amount of the catalyst. If a powder mixture was used, the decomposition proceeded to 100%. The initial fast process, which was linear in time, was described by the equation

$$p = mkt \qquad (1)$$

and the break-down stage by

$$1-(1-\alpha)^{1/2} = kt \qquad (2)$$

(m = weight of AP).

The activation energy of the catalytic reaction was found to be 33.2 and 31.5 kcal, respectively. From studies using oxide containing ^{18}O it turned out that the oxide does not take part chemically in the process. The authors also examined the catalytic effects of manganese oxides of various compositions. MnO_2 was 5 times more effective than MnOOH and 10 times more effective than Mn_2O_3. Mn_3O_4 at 153.5 °C did not show accelerating effect. The MnO_2-catalysed decomposition of AP was also studied by HERMONI and SALMON [4]. The activation energy of the reaction in the temperature ranges 170—200, 200—240 and 249—272 °C was 28, 34 and 48 kcal, respectively. KURATANI [5] studied the catalytic effect of MnO_2 (1%) in the high temperature decomposition of AP above 310 °C, and obtained an activation energy value of 31.0 kcal. In both works the kinetic analysis was made with equation (2). The lowest temperature of explosion of AP in the presence of MnO_2 was 265 °C.

Iron(III) oxide

Iron(III) oxide proved to be a less active catalyst than manganese dioxide; this is primarily of interest because iron oxide is one of the most frequently used catalysts in AP-containing propellants.

Below 240 °C in air at atmospheric pressure the decomposition of AP was scarcely changed by iron(III) oxide, even in large amounts [6]. Its effect was observed

primarily in that the transformation during the decomposition was 40—45% instead of 30—33%

In the presence of a small amount of oxide above 240 °C, up to 25—28% conversion, the reaction had practically the same rate as in the case of the pure salt. The effect of a greater amount of iron oxide (1:1 molar ratio) was not only a higher conversion but also almost a doubling of the reaction rate, and this latter further increased with increase of the amount of iron oxide. The α *vs.* t curves had an autocatalytic character, and the τ_{max} values practically agreed for the different compositions. The values of the rate maximum w_{max} were greatest for a powder mixture containing much iron oxide. The decomposition proceeded up to 60—95%.

For the determination of the rate constants the Prout—Tompkins equation

$$\log \frac{\alpha}{1-\alpha} = kt + C \tag{3}$$

and the Avrami—Erofeyev equation

$$-[\log (1-\alpha)]^{1/3} = kt + C \tag{4}$$

proved the most suitable in the present case. Activation energies of 32 kcal and 30.5 kcal were found for the acceleration stage and the break-down stage, respectively.

In this same temperature region, SHIDLOVSKII [7] obtained a value of 41.0 kcal for the activation energy of the catalytic decomposition. The experimental conditions differred from the above in that the measurements were made in vacuum.

Under adiabatic conditions the activation energy of the reaction was found to be 34.3 kcal [8].

The effect of iron(III) oxide on the high temperature decomposition of AP was studied in the range 320—380 °C [6]. The α *vs.* t curves were divided into two sharply separated stages. The initial fast stage was completely independent of the temperature of reaction and the amount of oxide, and depended only on the quantity of AP. In this stage the reaction proceeds to about 30%. Equation (4) was found to be the most suitable for the kinetic evaluation of the second stage. Depending on the amount of catalyst, the value of the activation energy varied between 22 and 30.8 kcal.

With the differential scanning calorimetric method, WAESCHE and VENOGRAD [9] obtained an activation energy of 48.0 kcal at 300—350 °C.

The explosion of AP in the presence of iron(III) oxide occurred at a substantially lower temperature than in the pure state [10]. The lowest temperature of explosion decreased gradually with the increase of the amount of catalyst. The 1:1 molar mixture exploded at the lowest temperature, at 300 °C.

Copper(I) oxide

The effect of copper(I) oxide, primarily on the inducing of the explosion of AP, was studied by JACOBS and KUREISHY [11, 12]. In the presence of copper(I) oxide the AP exploded even at 248 °C. Two factors play a part in the occurrence of the explosion: the heat of reaction liberated during the oxidation of the oxide, and the catalytic effect of the copper(II) oxide formed.

The amounts of both AP and the catalyst exerted an effect on the occurrence

of the explosion: in the presence of a small amount of catalyst (22 mole %) the explosion took place at a higher temperature, probably because the reaction heat evolved during the oxidation of the catalyst was not sufficient for a significant increase of the rate of decomposition.

The above was confirmed with the help of a thermocouple placed in the sample. In the presence of greater amounts of catalyst a well-measurable temperature increase was observed in the sample. From a kinetic analysis of the reaction leading to explosion, an activation energy of 28 kcal was obtained, whereas from the temperature dependence of the induction periods prior to the explosion a value of 28.1 kcal was found.

The large catalytic effect of copper(I) oxide was also observed by other authors [5, 7]. Fairly large deviations were shown in the activation energy values for the catalytic reaction.

Copper(II) oxide

While the decomposition of pure AP is immeasurably slow below 200 °C, in the presence of copper(II) oxide it already begins at 180 °C after an induction period of about 10—15 hours [13]. The reaction was followed in air by measuring the amount of gas. The induction period varies on increase of the amount of copper oxide. The shortest induction period was found with a 16:1 molar mixture. The catalytic effect of copper oxide could be observed even when present in only 0.5 weight%. The reaction has an autocatalytic nature. The conversion was 50—60%. The mathematical approximations for the α *vs.* t curves were made with the Prout—Tompkins and Avrami—Erofeyev equations. The activation energy values for the catalytic reaction were 28.9—32.9 kcal. At 200—240 °C the decomposition of AP proceeded at a higher rate than the previous up to 80—90%, but with a considerably larger activation energy of 40—42 kcal.

With a further increase of the temperature range for the reaction, to 240—289 °C, the activation energy for the decomposition increases to 47.7 [14] and 53.5 kcal [7]. This result is certainly connected with a change in the mechanism of the catalytic reaction. It seems also probable that in this temperature interval the reaction is already very fast, and so it is fairly difficult to ensure isothermal conditions.

In addition to the large increase in the rate of decomposition, it is relevant that above 250 °C in the presence of a sufficient amount of oxide the AP exploded after an induction period of only 2—3 minutes [13]. On addition of 0.15 weight% copper oxide, the explosion occurred already at 270 °C. The induction period was the shortest in the 16:1 molar mixture and this composition exploded at the lowest temperature, 251 °C. If a larger amount of catalyst was used (1:5 molar ratio), merely a degenerate explosion occurred. From the temperature dependence of the induction periods, activation energy values of 29—31 kcal were obtained for the explosion of mixtures of different compositions [13, 5]; these values are substantially smaller than those obtained for the catalytic decomposition process in the same temperature range. It is presumably of importance for the different activation energy values that up to the occurrence of the explosion (during the induction period) only 20—26% of the AP decomposed. This activation energy value agrees essentially with that determined for the slow decomposition at 180—200 °C, and hence it was assumed that in both cases the same decomposition mechanism is dominant [13].

Considering that the activation energies of the decomposition of AP catalysed by MnO_2 [3], Fe_2O_3 [6] and CuO [13], especially at lower temperatures, were practically the same as the activation energy of the electron transfer process in the decomposition of AP, it was rightly possible to assume that the oxides accelerate the decomposition of AP by an electron transfer process, and the role of the oxides consists in promoting the electron transfer from the perchlorate anion to the ammonium cation, and in the inhibition of the back reaction [3]. On this basis it was expected that the effectivity of an oxide would depend sensitively on its electronic structure, and that the rate of the catalytic reaction would change with the concentrations of electrons and defect-electrons on the oxide, or in other words with the electron acceptor ability. CuO appeared particularly suitable to check this working hypothesis since its electrical conductivity can be increased and decreased by the incorporation of small amounts of ions of different valencies. With this aim, CuO was doped with 1 mole% Li_2O and with 1 mole% Cr_2O_3 [13]. With the copper oxide doped with lithium oxide, at 170—200 °C the decomposition of AP began sooner and the reaction proceeded much more quickly than in the presence of the pure oxide. In contrast, the chromic oxide doping increased the induction period and slightly decreased the reaction rate. The activation energies were essentially unaffected by the doping of the copper oxide and were 29—32 kcal.

The effects of the doping are presented in Fig. 1.

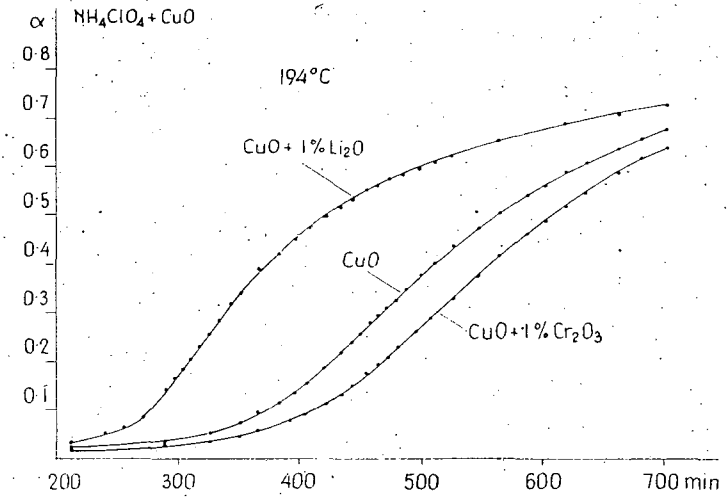

Fig. 1. Effect of doping with CuO on the catalytic decomposition of AP

At 200—240 °C the doping of the copper oxide with foreign ions did not produce a clear-cut change; this was explained, on the basis of the activation energy increase observed in this temperature interval, by the fact that the catalysed reaction in this stage no longer proceeds by the electron transfer mechanism. However, the effect of doping the catalyst could be observed in the course of the copper oxide initiated explosion of AP. The AP exploded at the lowest temperature in the presence of

the copper oxide doped with lithium oxide, and at the highest temperature with the chromic oxide doped catalyst. Nevertheless, at the temperature where all three mixtures exploded, there was scarcely any difference in the induction periods (Fig. 2). The activation energy values were 29—31 kcal in these cases, too.

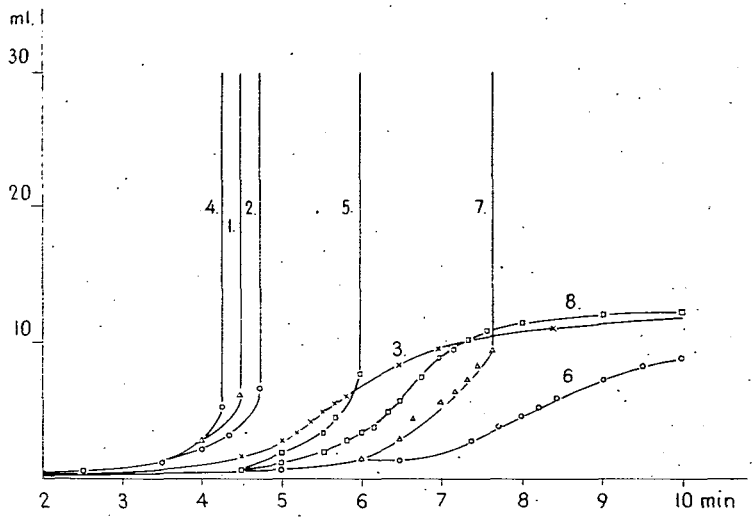

Fig. 2. Effect of doping with CuO on the ignition of AP. AP:CuO mole ratio 5:1 CuO + 1% Cr_2O_3: 1. 269.6 °C; 2. 266.5 °C; 3. 264.0 °C; CuO + 1% Li_2O: 4. 269.7 °C; 5. 262.2 °C; 6. 257.2 °C; 7. 260.0 °C; 8. pure CuO. 264.0 °C

Nickel(II) oxide

The effect of nickel on the stability of AP was first studied in detail by HERMONI and SALMON [4] by measuring the weight losses and the pressures of permanent gases at 200—260 °C. If powder mixtures were used, almost complete decomposition of the AP was observed. The final pressure of non-condensing gases varied with the quantity and quality of the oxide. The evaluation of the α *vs.* t curves was carried out with equation (3). A decomposition consisting of two sections was obtained, the rate in the first stage being the greater; however, this was not evaluated kinetically.

The activation energies of the catalytic reaction at 170—200°C and at 210—240°C were 33 and 43 kcal, respectively. The increase of the value of the activation energy is explained by a change of mechanism. The kinetic studies by SHIDLOVSKII [7] led to essentially the same results.

The effect of NiO, similarly to that of CuO, depended on the electrical properties [15]. It began first below 200°C in the presence of nickel oxide doped with lithium oxide. Incorporation of chromic oxide into the nickel oxide decreased the extent of catalysis significantly. The effect of doping the nickel oxide showed up, in general, in the initial section of the decomposition (the induction period, the stage of acceleration). Below 200 °C the decomposition proceeded to about 55%. The Prout—Tompkins equation proved most suitable in the evaluation of the α *vs.* t curves, but the Avrami—Erofeyev equation also gave satisfactory results. The value of the

activation energy was 30—35 kcal. Apart from the doping, the effect of the nickel oxide catalyst also changed with the temperature of pre-treatment [15]. With the increase of the ignition temperature of the oxide, in the range 500—1000 °C, the catalytic effect decreased considerably. Such a large effect of the temperature of pre-treating the oxide was not observed in the case of any other catalyst. A part may be played in the decrease of the catalytic effect not only by changes in the extent of the surface of the catalyst but also by a significant modification of the defect and the electronic structure of the nickel oxide.

In experiments with nickel oxide, BOLDYREV *et. al.* [16], however, showed that its catalytic effect at 250—300 °C depends on the extent of the BET surface of the oxide.

Chromic oxide

HERMONI and SALMON [4] also investigated the effect of Cr_2O_3 in the manner reported above. The characteristics of the catalytic reaction were the same as in the presence of NiO. The activation energies at 210—230 °C and at 250—275 °C were 26.7 and 37.7 kcal, respectively. An outstandingly large value of the activation energy, 68 kcal, was obtained by the adiabatic method [8].

Interesting results were produced by studying the effect of the electrical structure of the Cr_2O_3 [17]. The latter was doped with zinc(II), nickel(II) and titanium(IV) ions. The incorporation of the foreign ions was promoted by firing of the samples at 1100 °C. The high temperature treatment resulted in a considerable decrease of the effectiveness of the chromic oxide. The course of the slow decomposition of AP at 230 °C up to about 30% transformation was almost the same in the case of both pure and doped chromic oxide. A noticeable difference appeared only

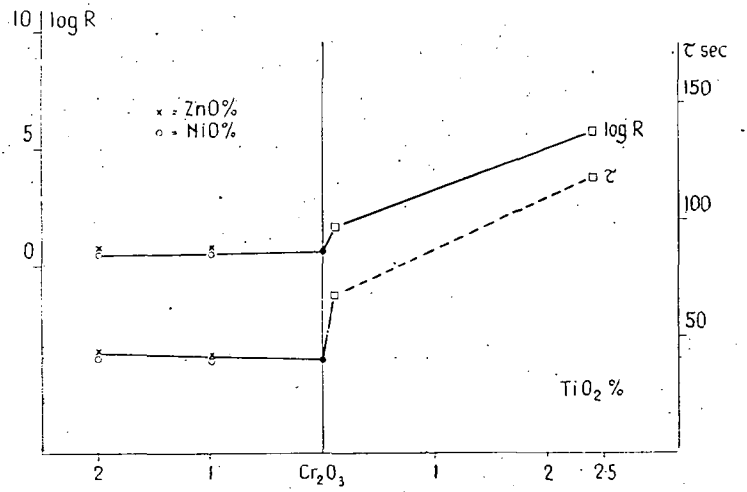

Fig. 3. Effect of doping on the electric resistivity of Cr_2O_3 and on the induction period for the ignition of AP

in the subsequent stage, where the slowest decomposition occurred in the presence of chromic oxide doped with 2.5% titanium dioxide.

At higher temperatures, the AP exploded even in the presence of a small amount of chromic oxide (100:1 molar ratio) at 295 °C. The explosion temperature decreased with increase of the amount of chromic oxide and then reached a limiting value. The lowest explosion temperature was 251 °C (AP:Cr_2O_3 molar ratio 1:1); while with a 10:1 molar mixture it was 275 °C. The incorporation of zinc and nickel oxides into the chromic oxide practically did not affect the behaviour of the latter. However, doping with titanium dioxide produced a significant change; compared with the effect of pure chromic oxide, it increased both the explosion temperature of the AP and the time till the explosion. The activation energy values calculated from a temperature analysis of the induction periods were 29—31 kcal in these cases, too. The effect of doping the chromic oxide on the induction period of the explosion of AP is shown in Fig. 3.

Cobalt(II, III) oxides

Cobalt oxide is likewise an effective catalyst of the decomposition of AP. Using the method reported above, HERMONI and SALMON [4] obtained an activation energy of 33 kcal for the catalytic decomposition at 170—200 °C. At 210—230 °C they obtained a value of 42 kcal, and SHIDLOVSKII [7] one of 38.3 kcal.

In the presence of cobalt oxide AP exploded at 241 °C. The activation energy value was 45.8 kcal. The value of the induction period preceding the explosion decreased with increase of the gas pressure.

Carbon and copper chromite

It is practical to consider studies of the effects of carbon and copper chromite together, for in many cases the two substances are applied jointly. Copper chromite (together with or without carbon) is the catalyst most generally used in the composite propellant based on AP to increase the rate of ignition. In spite of this, it is surprising that relatively few studies have been carried out in connection with its effects on the slow decomposition of AP.

The decomposition of AP below 240 °C was practically not affected by active carbon [18]. After the reaction, the carbon remained in an unchanged state. Between 240 and 260 °C the decomposition began without an incubation stage and the breakdown section was substantially longer than in the case of the pure salt. Above 260 °C the decomposition accelerated and a mild explosion was produced. From the temperature dependence of the times up to explosion an activation energy of 40 kcal was calculated. Experiments were also made to determine the critical temperature of explosion and the critical amount of AP.

With an adiabatic method they determined an activation energy of 52.5 kcal for the decomposition catalysed by carbon [8].

At 216—277 °C copper chromite (Harshaw, 0202P product) increased the rate of decomposition of AP altogether by 50%. The value of the activation energy was the same as in the decomposition of pure AP, 31 kcal [14]. A substantially greater effect on the high temperature (280—340 °C) decomposition of AP, was

exerted by copper chromite. Increase of the amount of catalyst in the range 0.5—5 weight% increased the rate constant of decomposition, but the addition of carbon to the copper chromite hardly affected it. The α *vs.* t curves obtained from gravimetric measurements were of a break-down nature; their mathematical analyses were carried out with equation (2) ($n=2$). The value of the activation energy was 48 kcal. A similar activation energy was also obtained in this temperature region for the decomposition of pure AP.

The explosion of the AP occurred first at 290 °C (5% catalyst). From the temperature dependence of the induction periods at 290—440 °C surprisingly low activation energies of 12—14 kcal were obtained.

With the adiabatic method, using different amounts of copper chromite, activation energies of 40—46 kcal were determined [8]. In agreement with the above, it was found that in the presence of catalyst the autocatalytic nature of the decomposition is lost.

Zinc oxide

Similarly to the above, a surprisingly large acceleration of the reaction occurred in the presence of zinc oxide; this approximated, and in some respects exceeded the effects of the most effective transition-metal oxide [19, 20].

On the admixture of only small amounts of zinc oxide (50:1 molar ratio), the decomposition of AP retained its autocatalytic nature but proceeded not to 30% but, instead, to about 75—80%. The zinc oxide decreased the value of the induction period (τ_0), the effect being more pronounced with increase of the amount of zinc oxide. The measurements were evaluated using the Prout—Tompkins and the contracting cube equations. The activation energy values at 200—240 °C for the various compositions were around 30 kcal.

Above 240 °C the catalytic reaction proceeded extremely violently and, after a fairly long induction period of 10—25 minutes, the AP exploded. The induction period increased slightly with increase of the amount of zinc oxide up to a 1:1 molar ratio. The activation energy values were prectically the same as above [19, 20, 5].

The lowest temperature of explosion of AP in the presence of zinc oxide was 233 °C (100:1 and 50:1 molar ratios). This means that the zinc oxide decreased the temperature of explosion of the AP by more than 200 °C.

Detailed studies were also carried out with doped zinc oxide samples. The AP:oxide molar ratio was 16:1. On the incorporation of 1 mole% aluminium oxide the catalysed decomposition began sooner and the reaction itself proceeded more quickly. Doping the zinc oxide with lithium oxide increased the induction period and decreased the reaction rate. However, in these cases the decomposition of AP proceeded to 85—95%. The value of the activation energy in the presence of the doped catalysts did not change. On the other hand, doping of the zinc oxide did alter the induction period of the explosion of AP; it decreased on the incorporation of aluminium oxide and increased on the incorporation of lithium oxide.

Investigation of the mixture during and after the reaction yield valuable data. It was observed that in the presence of zinc oxide the AP partially melted. The solid residue contained water soluble zinc salt.

The melting of the AP was interpreted by the reaction of the zinc oxide and the

AP at the temperature of decomposition:

$$ZnO + 2\ NH_4ClO_4 = Zn(ClO_4)_2 + 2\ NH_3 + H_2O,$$

the zinc perchlorate formed yielding a eutectic of lower melting point with the remaining AP.

The addition of zinc perchlorate to AP supported the above explanation; this led to the partial melting of the AP and to the increase of the decomposition rate observed in the presence of zinc oxide [20, 21].

The large catalytic effect of zinc oxide and the reaction between zinc oxide and AP were confirmed by many later studies [5, 22—24]. BOLDYREVA [25] proved the formation of zinc perchlorate by infrared spectroscopic investigation.

Cadmium oxide

Cadmium oxide also exerted a considerable accelerating influence on the decomposition of AP [26], although its effect was smaller than that of zinc oxide. The beginning of decomposition, especially in the presence of larger amounts of oxide, was preceded by an unusually long induction period. A catalytic effect was primarily shown with smaller concentrations (100:1 and 16:1 molar rations). From kinetic measurements at 200—240 °C an average activation energy of 28 kcal was obtained.

Cadmium oxide reduced the lowest temperature of explosion of AP by about 180 °C. The 10:1 molar ratio mixture exploded at 260 °C. However, here too, the induction period preceding explosion was unusually long, being 17 minutes at 270 °C (16:1 molar ratio). Since cadmium oxide contains a significant amount of excess cadmium, it was conceivable thet the cadmium excess incorporated into the oxide was responsible for the large accelerating effect. The answer to this question was provided by doping experiments.

CIMINO and MAREZIO [27] demonstrated with X-ray studies that on the incorporation of indium the number of interstitial cadmium atoms gradually decreases, and becomes zero at an indium oxide content of about 0.15 mole%. Since the behaviour of cadmium oxide prepared by the method of CIMINO and MAREZIO, and containing the critical amount of indium oxide, was essentially unchanged, the possibility of the cadmium excess being responsible for the catalytic effect of cadmium oxide was ruled out.

In experiments carried out below 240 °C it was observed that if the AP contained less cadmium oxide than a 10:1 molar ratio, then the originally greyish-black mixture began to lighten during the induction period and in the acceleration stage the colour of the cadmium oxide could already hardly be seen. The situation was similar in experiments carried out above 250 °C, too, but here melting of the substance in certain parts of the tablet could also be observed. This indicated that a reaction between the AP and the cadmium oxide took place, analogous to that in the case of zinc oxide. Before the explosion, the cadmium oxide reacted either in part or completely with the AP. Considering the extremely long induction period, it was concluded from these results that AP explodes in the presence of cadmium oxide only when the reaction between the two substances has proceeded to a definite extent. The reaction between AP and cadmium oxide was confirmed by chemical analyses [26] and IR spectroscopic studies [25].

Magnesium oxide

Among the insulating oxides, an effect increasing the reaction rate was observed [28, 29, 4] only in the case of magnesium oxide. The extent and rate of the decomposition of AP depended extremely sensitively on the temperature and the quantity of magnesium oxide. An acceleration effect occurred in the presence of small amounts of MgO. The use of much MgO (AP:MgO molar ratio 2:1) hindered the course of the AP decomposition. HERMONI and SALMON [28] found that at 170—230°C the decomposition is complete, but at 240, 250 and 280°C it proceeded only to 20, 4.81 and 23%, respectively. The rate of decomposition of the 2:1 AP:MgO mixture in the range 200—280°C was the greatest at 230 °C and the least at 240—250 °C. From kinetic measurements at 206—235°C in the presence of a little oxide, an activation energy of 29—31 kcal was obtained for the reaction [28, 29, 4]. Above 300°C even a small amount of magnesium oxide delayed the beginning of decomposition significantly [29]. After a reaction time depending on the temperature and the amount of oxide, the inhibition changed to catalysis. Also here the catalytic effect was more pronounced when a small amount of oxide was used. This is supported, among others, by the fact that while the 100:1 molar mixture exploded at 270°C, the 25:1 mixture exploded only at 336°C (Fig. 4). Evaluation of the temperature dependence of the induction period of the explosion led to an activation energy of 26—30 kcal. From a kinetic analysis of the decomposition leading to explosion using the equation

$$\log p = kt + C$$

an activation energy of 33.5 kcal was obtained.

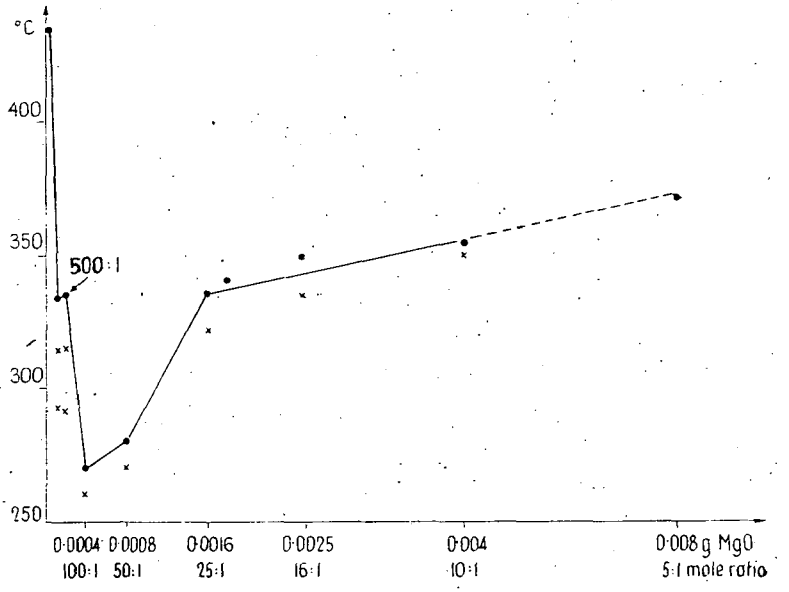

Fig. 4. The minimum ignition temperature of AP as a function of the amount of MgO

From the behaviour of the mixtures it was clear that the AP reacts with the magnesium oxide. As a result of the reaction, magnesium perchlorate is formed and the AP partially melts.

Titanium and tin dioxides

Pure titanium dioxide can be considered to be a practically inactive substance in the decomposition of AP [5, 17]; below 240 °C the decomposition of AP in the presence of titatium dioxide differs from the decomposition of pure AP only at the end of the break-down stage. The situation was similar in experiments carried out at 248.5 °C. The rate constant of the acceleration and break-down stage agreed with the rate constants of pure AP, and their temperature dependences were essentially the same, too. Activation energy values of 30 and 29.5 kcal were found [17]. The effect of titanium dioxide remained slight at 300—440°C, too, and the temperature of the explosion of AP was reduced from 436 °C only to 420—425 °C. The situation was essentially similar if 1% tungsten(VI) oxide (electron concentration increase) or 1% nickel oxide or aluminium oxide (electron concentration decrease) were incorporated into the titanium dioxide. However, an extremely large change occurred when the titanium dioxide was doped with chromic oxide. Even 0.1 mole% chromic oxide in the titanium dioxide led to a noticeable change, while on the incorporation of 1 mole% chromic oxide the explosion temperature of AP decreased by about 150 °C. The effect of the amount of chromic oxide was especially expressed in the case of mixtures containing little titanium dioxide + chromic oxide catalyst (AP:oxide molar ratio 10:1); on the incorporation of only 3.8×10^{-4} g chromic oxide into the titanium dioxide the AP exploded at 290°C. The activation energy of the process leading to the explosion varied from 29 to 32 kcal for the different compositions.

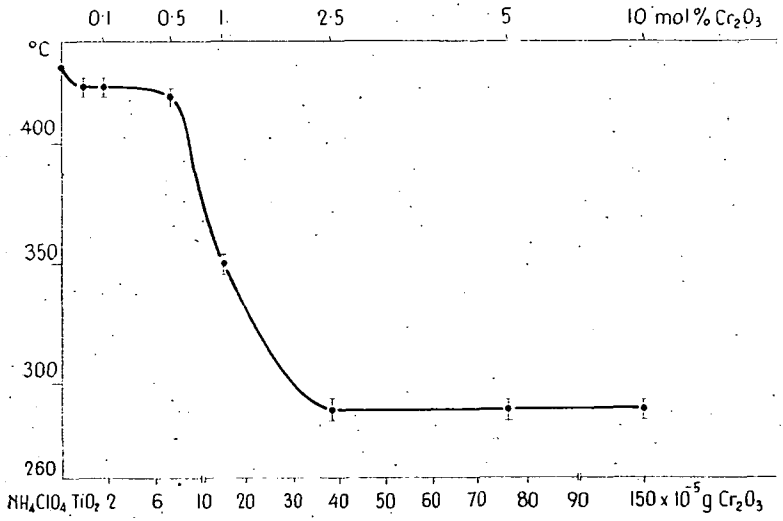

Fig. 5. The minimum ignition temperature of AP as a function of the Cr_2O_3 content of TiO_2

The effect of the amount of chromic oxide incorporated into the titanium dioxide on the lowest temperature of explosion of the AP is shown in Fig. 5.

On appraisal of the large catalytic effect of titanium dioxide doped with chromic oxide, it must be taken into consideration that the chromic oxide added to the titanium dioxide cannot be considered as "free" oxide; as a consequence of the high temperature of pre-treatment of the catalyst, the chromic oxide is incorporated into the surface layer of the titanium dioxide. Study of the mechanism of incorporation of the chromic oxide led to the result [30] that, as a consequence of the oxidation (valence inductivity) accompanying the incorporation of the chromic oxide, the chromium becomes partially tetravalent and partially pentavalent.

A study of the effect of tin dioxide led to similar results [31]. Pure tin dioxide exerted only an extremely slight effect on the decomposition of AP at various temperatures. The lowest temperature of explosion of AP was reduced in all by 40 °C. The effectiveness of the catalyst, however, improved considerably on doping it with 0.1—1 mole% chromic oxide (Fig. 6).

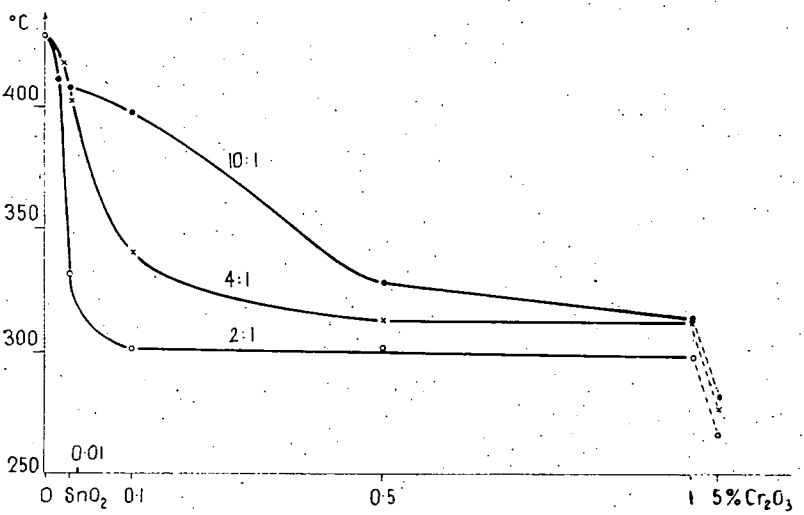

Fig. 6. The minimum ignition temperature of AP:SnO_2 mixtures of different mole ratios as a function of the Cr_2O_3 content of SnO_2

From a detailed physical and chemical investigation of the oxide mixture, it turned out that, here again, on incorporation the chromium ions were oxidized to higher valencies, which were stabilized by the tin dioxide lattice.

Other oxides

With regard to other oxides very few data can be found in the literature. According to BIRCUMSHAW [2] aluminium oxide can be considered as a practically inactive substance and calcium oxide acts as an inhibitor.

According to the most recent measurements, very slight effects on the stability of AP are exerted by tungsten(VI), molybdenum(VI) and vanadium(V) oxides [32]. All three substances belong to the group of *n*-conducting semiconductors.

Table 1

Kinetic data for the decomposition of AP catalysed by oxides

Oxides	Characteristics of AP	Amount of oxides, mole%, (mole ratio)	Temperature range °C	Methods	Kinetic equation	Validity $\alpha =$	Activation energy $\left(\frac{\text{kcal}}{\text{mole}}\right)$	Log A (min^{-1})	Ref.
MnO_2	2× cryst	34—90	137—162	*p*, vacuum	C—2		31.5		[3]
		10	177—212		$p = mkt$		33.2		
	Baker								
	1× cryst	13	170—200	*w*, vacuum	C—3	0.2—0.9	28.0	8.60	[4]
		13	200—240	*p*, vacuum	C—3	0.2—0.9	34.0		
		13	249—272	*p*, vacuum	C—3	0.2—0.9	48.0		
		5(s)	214—245	*w*, in air	A—E		33.7	12.7	[7]
	3× cryst	1	317—340	*p*,	C—2		31.0	7.76	[5]
Fe_2O_3	Merck	20	249—268	*v*, in air	P—T	0.01—0.27	35.6		[6]
		20			P—T	0.37—0.89	30.9		
		20			first order	0.09—0.83	28.2		
		50			P—T	0.01—0.22	28.5		
		50			P—T	0.41—0.92	29.0		
		50			first order	0.16—0.83			
		50:1	320—377		C—3	0.32—0.81	30.9		
		20:1				0.32—0.88	25.7		
		8:1				0.33—0.85	22.0		
		5(s)	250—296	*w*, in air	A—E		41.0	14.42	[7]
	88—124μm	4.9			adiabatic		34.3		[8]
	43—61μm	4.8					36.6		
Cu_2O	BDH	4.56	240—270	*p*, 250 torr N_2	$p = Ce^{kt}$		29.0		[11]
	3× cryst	1.0	260—280	*p*,	$\log = kt$		36.0	12.54	[5]
		5(s)	250—270	*w*, in air	A—E		45.5	17.15	[7]
CuO	Merck								
	2× cryst.	5:1	180—200	*p*, air	P—T	0.0—0.36	32.7		[13]
		5:1	180—200		A—E	0.0—0.58	32.9		
		1:1	180—200		P—T	0.0—0.36	30.0		
		1:1	180—200		A—E	0.0—0.58	28.9		
CuO		5:1	180—200		P—T		32.1		
$+1\%\ Cr_2O_3$		5:1	180—200		A—E		30.0		
CuO		5:1	180—200		P—T		29.2		
$+1\%\ Cr_2O_3$		5:1	180—200		A—E		31.7		
CuO		5:1	201—227		P—T		42.9		
		5:1	201—227		A—E		40.9		
		1:1	203—228		P—T		40.2		
		1:1	203—228		A—E		42.2		

Oxides	Characteristics of AP	Amount of oxides, mole %, (mole ratio)	Temperature range °C	Methods	Kinetic equaiton	Validity $\alpha =$	Activation energy $\left(\frac{kcal}{mole}\right)$	Log A (min^{-1})	Ref.
CuO +1% Li_2O		5:1	201—227		P—T		41.2		
CuO +1% Cr_2O_3		5:1	201—227		P—T		37.1		
Ni_2O_3	Baker	13	170—200	*w*, vacuum	C—3		33.0	12.48	[4]
	1× cryst	13	210—235	*p*, vacuum	C—3		43.0		
		13	245—265	*p*, vacuum	C—3		40.2		
		5(w)	270—296	*w*, in air	A—E		49.2	17.8	[7]
Co_2O_3 + Co_3O_4	Baker	13	170—200	*w*, vacuum	C—3		33.0	13.95	[4]
	1× crys)	13	210—230	*p*, vacuum	C—3		42.0		
		5(w)	215—245	*w*, in air	A—E		38.3	14.87	[7]
Cr_2O_3	Baker								
	1× cryst.	13	210—230	*p*, vacuum	C—3		26.7	9.00	[4]
		13	250—275	*p*, vacuum	C—3		37.7		
		5(*w*)	260—309	*w*, in air	A—E		30.1	9.90	[7]
	BDH	0.85	306—348		C—3		31.3	8.80	[14]
		4.8			adiabatic		68.0	27.3	[8]
CuO + Cr_2O_3	BDH	0.5—5	207—277	*w*, in air	A—E		31.6	11.82	[14]
		0.5—5	283—315		C—2		47.7	15.67	
		2.9			adiabatic		40.0	13.8	[8]
		4.8					43.0	16.5	
		4.8	250—308				46.0	17.7	
		0.5—5	300—350		C—2		48.0		[9]
Active carbon	2× cryst	3—17	195—240	*p*, vacuum	P—T		32.1		[18]
		2.5			adiabatic		52.5	19.9	[8]
ZnO	Merck	16:1	215—231	*v*, in air	P—T	0.0 —0.15	29.7		[19, 20]
		16:1			P—T	0.15—0.85	33.7		
		16:1			C—3	0.1 —0.8	33.3		
		50:1			P—T	0.0 —0.15	31.3		
		50:1			P—T	0.15—0.85	22.5		
		50:1			C—3	0.1 —0.8	29.5		
		100:1			P—T	0.0 —0.15	24.0		
		100:1			P—T	0.0	26.0		
		100:1			C—3	0.1 —0.8	27.9		

Oxides	Characteristics of AP	Amount of oxides mole %, (mole ratio)	Temperature range °C	Methods	Kinetic equation	Validity $\alpha =$	Activation energy $\left(\frac{\text{kcal}}{\text{mole}}\right)$	Log A (min^{-1})	Ref.
CdO	Fluka 2× cryst	16:1	206—233	p, vacuum	P—T	0.0 —0.18	26.7		[26]
MgO		13.5 (w)	215—230	p, vacuum	C—3		31.4	11.2	[28]
			215—230		P—T		29.2	10.8	
	Fluka 2× cryst	16:1	206—231	p, vacuum	P—T	0.01—0.43	30.3		[29]
					A—E	0.01—0.46	28.5		

A—E = Avrami—Erofeyev equation
P—T = Prout—Tompkins equation
C—3 = "Contracting cube" formula, $n = 3$
C—2 = "Contracting cube" formula, $n = 2$
p = pressure measurements
w = weight-loss measurements
v = volume measurements
s = weight%

Effects of various salts on the stability of AP

The decomposition of AP is catalysed not only by metal oxides but also by many metal salts. The first intensive kinetic study dealt with the effects of silver, copper and iron perchlorates [33]. Silver perchlorate proved the most effective additive; even 0.001 mole% increased the rate of decomposition of AP below 240 °C, and the effect increased with increase of the amount. The catalysed decomposition remained of an autocatalytic nature and stopped after about 40—45% transformation. The value of the activation energy was 28 kcal.

Copper(II) and iron(III) ions exerted somewhat less effects. The rate and the activation energy of the catalytic reaction depended on the preparation of the AP—perchlorate salt mixture. The reaction proceeded at a higher rate and with a lower activation energy if copper perchlorate was evaporated with the AP solution than if the solid substances were mixed together. A part in bringing about a greater lability may be played (in addition to the more homogeneous distribution of the additive) by the incorporation of the copper ion and the change in the defect structure of the AP.

In the presence of 1 mole% of the above perchlorates the explosion of AP occurred at the following temperatures:

copper perchlorate 269 °C
silver perchlorate 274 °C
iron perchlorate 276 °C.

From the temperature dependence of the times up to the explosion, a few kcal smaller activation energy values were found than for the slow catalysed decomposition. These data show convincingly that the effects of the above additives in bring-

ing about the explosion of AP approach and even exceed the effects of the most active oxides.

From later studies it turned out that zinc, cadmium and magnesium perchlorates also effectively accelerate the decomposition of AP [34, 21, 26]. From the point of view of the mechanism of decomposition of AP, this result is a very important observation, since it shows that not only ions capable of electron transfer are able to catalyse the decomposition of AP.

In the presence of any of the three substances, a large rate increase was observed even at 200—240 °C; the induction period decreased significantly and the decomposition proceeded to 100%. In the presence of the cadmium or magnesium salt the decomposition was autocatalytic, but the zinc salt brought about a change to breakdown nature.

An interesting observation was that in the AP:perchlorate salt composition range 100:1—1:1 the decomposition started in every case in the mixture containing the less additive. The acceleration stage of the decomposition, however, was shorter than in the presence of larger amounts of cadmium and magnesium perchlorates. In the 5:1, and particularly in the 1:1 mixture, the rate of decomposition was considerably lower than *e.g.* in the 100:1 molar mixture. The activation energies of the decompositions catalysed by cadmium and magnesium ions were about 28—32 kcal. A larger value, 37 kcal, was obtained in the presence of zinc perchlorate. Recent kinetic measurements on the effect of magnesium perchlorate, at 280—320 °C, resulted in higher values, 44—47 kcal/mole, for the activation energy [35]. This is presumably due to the higher temperature range.

In the optimum (100:1) molar mixture the explosion of AP occurred at the following temperatures:

zinc perchlorate	240 °C
cadmium perchlorate	260 °C
magnesium perchlorate	270 °C.

Fig. 7 characterizes the great effect of zinc perchlorate.

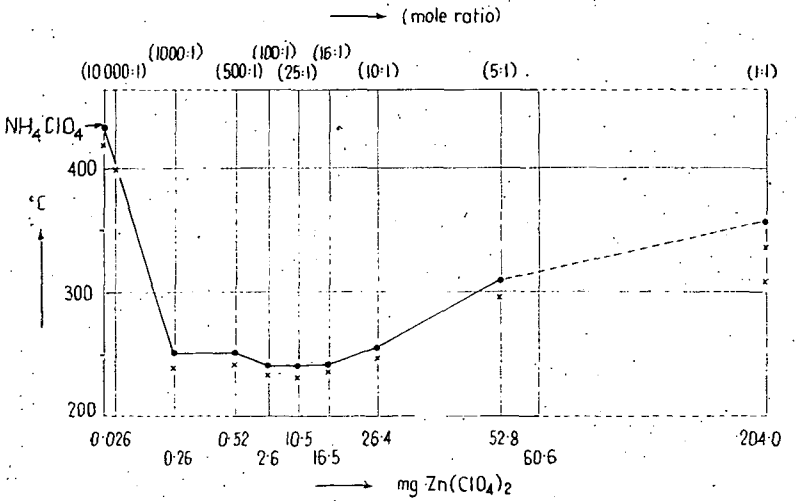

Fig. 7. The minimum ignition temperature of AP as a function of the amount of $Zn(ClO_4)_2$

On addition of even 0.1 mole% zinc perchlorate to AP, it explodes at a 190°C lower temperature than in the pure state. Increase of the amount of the perchlorate salt in all three cases proved unfavourable. At 240—290°C the activation energy of the reaction preceding the explosion was 27—32 kcal.

As regards the evaluation of the effects of the additives, it was important that in the presence of the above perchlorates the solid mixture partially melted already below 240 °C. Taking into account the melting points of the compounds concerned, this can only be explained by the formation of a melting eutectic. The effect of a salt increased in the order Mg, Cd, Zn; this corresponds to the increase in polarizing power of the metal ions.

It should be noted that the chloride salts of the metal ions in question exerted very similar effects on the stability of AP as the perchlorates. The partial melting of the AP could be observed here, too. However, the acceleration of AP decomposition did not occur with the use of zinc, cadmium and magnesium sulphates, and in their presence the AP did not melt.

The knowledge of the phase diagram of the AP+lithium perchlorate system gave the possibility of studying the thermal behaviour of AP in the molten phase. The eutectic mixture contained 35.5 mole% AP and its melting point was 182 °C [36].

Below 240 °C the rate and extent of the decomposition decreased with increasing amount of lithium perchlorate. The highest extent of decomposition (90—95%) occurred in the mixture containing 10 mole% lithium perchlorate. The eutectic mixture and mixtures containing lithium perchlorate in excess showed no noticeable decomposition up to 270 °C, even in 24 hours.

The high stability of the eutectic composition indicated that, although the lithium perchlorate brings about the melting of the AP, the formation of the eutectic also increases its stability to a large extent. It was interesting to observe that in a mixture containing excess AP as compared with the eutectic composition the amount of AP decomposed exceeded the excess amount of AP. This means that the decomposition of AP in the eutectic also began as a result of the decomposition of solid AP in the melt.

The activation energies of the decomposition of mixtures of various compositions (AP excess) agreed with the activation energy values determined for the decomposition of pure AP in the same temperature range.

The explosion of mixtures containing an AP excess was preceeded by decomposition, the extent of which decreased with increase of the amount of lithium perchlorate. The lowest temperature of explosion was 320—340 °C. The explosion of mixtures containing excess lithium perchlorate occurred at 290 °C after an unusually long induction period of 2—3 hours. The explosion was extremely violent, and was not preceded by evolution of gas. The effective catalysts of the decomposition of AP (Cu^{2+}, ClO_3^-, CuO, etc.) also decreased the stability of the eutectic considerably.

SHIDLOVSKII *et al.* [7] studied gravimetrically the effects of various salts (carbonate, chloride, oxalate) of manganese, cobalt, copper, iron, nickel and chromium on the stability of AP at atmospheric pressure. The manganese and cobalt compounds proved the most effective additives. The effects of the iron, nickel and chromium compounds appeared above 240 °C. In the case of the cobalt salts, the effect decreased in the order carbonate, oxalate, oxide, chloride. The activation energies of the catalytic reaction varied in the range 30—53 kcal. The effectiveness of a compound

was ascribed to the formation of its oxide: the more easily the oxide formed, the more effective was the compound.

Kinetic studies are also known with regard to the effects of iodide and bromide ions [33]. At 200—240 °C primarily the rate and extent of the acceleration reactions of AP are increased. The explosion of AP takes place at 260 and at 298 °C.

The lowest temperature and induction period of the explosion change sensitively with the concentration of the additive. With increase of the temperature the optimum amount of substance shifts towards lower concentrations.

Table II contains data for the decomposition of AP—salt additives. The effects of catalysts on the explosion of AP are collected in Table III.

Differential thermal analysis studies

In comparing the effects of additives, the fastest method involves thermal analysis procedures. The DTA measurements of LAND [38] refer to the effects of oxides. The order of effectiveness of oxides was the following:

Co Cu Ni Zn Mn Cd Pb Fe Ag Mg K Ba Na.

The temperature difference T_x between the crystallographic transition and the decomposition of the AP served as the basis for comparison. Since this value can be affected by numerous factors (particle size, catalyst surface, etc.), this order can only be regarded as of a qualitative nature. The development of a realistic picture is made difficult by the fact that LAND added the oxides to the AP in weight%.

RHEES and HAMMAR [39] studied the effect of modifying the AP surface, using a DTA method. Large effects were exerted by copper and magnesium oxides in particular, even in low concentration. The exothermic peaks in the decomposition of AP changed depending on the added substance.

LAND [40] studied the stability of AP in the presence of metal perchlorates and obtained the following series:

Cu Mn Zn Cd Pb Fe Mg Ag Ba K Na.

The amount of each perchlorate salt was 5 mole%. The preparation of the mixtures, however, gave a possibility for the incorporation of the metal ion into the crystal lattice of the AP and for the change of its defect structure, which likewise affect the stability of AP.

The effects of the perchlorates of transition metals (cobalt, nickel and iron) on the decomposition of AP were studied by BOLDYREV *et al.* [41] at 260—275 °C using a thermogravimetric method. The catalytic effectiveness decreased in the series cobalt, nickel, iron. The effects of the perchlorate salts were attributed to the actions of the oxides, for it was observed that before and during the decomposition of the AP the perchlorates decompose to Co_2O_3 and Ni_2O_3. The effectiveness of the above oxides practically agreed with that of the corresponding perchlorate and the above series was found again. Similarly to the earlier investigations [26, 34], the sulphates did not exhibit an acceleration effect; this was explained by their higher stabilities. The evaluation of the results is made difficult also by the fact that during the preparation of the mixture the additives might co-crystallise with the AP; and

as a result it is not possible to know what role the change of the defect structure of the AP (in this case the increase of the number of cation-free sites) plays in the awaited effect.

Using differential thermal analysis, OSADO and SAKAMOTO [42] studied the effects of various chlorides. Iron(III) and copper(II) chlorides showed the greatest

Table II

Kinetic data for the decomposition of AP catalysed by metal salts

Salts	Characteristics of AP	Amount of oxides mole %, (mole ratio)	Temperature range °C	Methods	Kinetic equation	Validity $\alpha =$	Activation energy (kcal/mole)	Log A (min^{-1})	Ref.
$AgClO_4$	p.a. 2× cryst.	0.1	209—235	v, in air	P—T	0.04—0.5	27.7		[33]
$Cu(ClO_4)_2$	p.a. 2× cryst.	1.0 5.0(*s*)	203—232 204—226	v, in air v, in air	A—E A—E	0.04—0.5	25.0 29.0		
$Fe(ClO_4)_3$	p.a. 2× cryst.	1.0 5.0	206—224 204—230	v. in air v, in air	A—E A—E		34.0 28.9		
$Zn(ClO_4)_2$	Fluka 2× cryst.	10:1	206—232 206—232	p, vacuum	first order	— 0.01—0.65	24.5 37.8		[21, 34]
$Cd(ClO_4)_2$	Fluka 2× cryst.	10:1	210—231	p, vacuum	A—T $\log p = kt$	— 0.0—0.22 0.0—0.2	28.7 29.3 33.0		[26, 34]
$Mg(ClO_4)_2$	Fluka 2× cryst.	10:1	201—231	p, vacuum	τ_0 P—T	 0.01—0.6 0.6—0.95 0.4—0.85 0.01—0.28	31.9 30.2 25.0 26.6 32.4		[34]
	Fisher	1.75	291—343	w, 740 torr N_2	C—2	0.1 —0.8	43.4		[35]
		6.6	286—318	w, 740 torr N_2	first order	0.27—0.89	45.2		
$LiClO_4$		10 30 50	210—240 210—240 210—240	v, in air v, in air v, in air	first order	0.1 —0.7 0.1 —0.7 0.1 —0.7	29.3 32.0 28.2		
NH_4I	p.a. 2× cryst.	0.1	206—235	v, in air	A—E	0.05—0.6	35.5		[34]
NH_4Br	p.a. 2× cryst.	0.1	206—235	v, in air	A—E	0.05—0.6	27.5		
$K_2Cr_2O_7$		1.67	312—339	w	C—2		47.7		[14]
$KMnO_4$		2.00	215—290			0.3	20.0		[46]
$CaCrO_4$			245—265				16.0		[46]

effects but calcium, magnesium and, to a smaller extent, sodium and potassium chlorides also shifted the second large exothermic peak, characteristic of the decomposition of AP, towards lower temperatures. The authors assumed that chemical reaction between the AP and the chlorides takes place with the formation of perchlorate salts which are effective with regard to the decomposition of AP. It should

Table III

Ignition of AP in the presence of additives

Additive	Characteristics of AP	Amount of additive mole %, (mole ratio)	AP mg	Minimum ignition temperature °C	Temperature range °C	Activation energy kcal/mole	Ref.
MnO_2	3× cryst	1.0	100	336		33.5	[5]
	1× cryst	5.0	150	265			[7]
	Baker 1× cryst	16(s)	100	310	310—335	34.3	[4]
Fe_2O_3		1:1	100	300			[10]
Cu_2O	BDH						
		6.7	30	248		28.1	[11]
		50.0	30	253		31	
	3× cryst	1.0	100	269		38.1	[5]
CuO	Merck	16:1	50	259	270—286	29.9	[13]
	2× cryst	16:1	100	270	265—286	31.2	
+1% Li_2O		16:1	100	260	260—286	30.0	
+1% Cr_2O_3		16:1	100	266.5	266.5—287	31.0	
		16:1	200	251	251—276	29.8	
	3× cryst	1.0	100	258		31.0	[5]
Ni_2O_3	Merck	1:1	100	253.2	255—275	29.1	[15]
Co_2O_3—Co_3O_4	Baker 1× cryst	30(s)	100	241	240—260	45.8	[4]
Cr_2O_3	BDH	1:1	100	251			[17]
	1× cryst	10:1	100	257	257—292	27.9	
+1% NiO		10:1	100	259	259—299	26.3	
+1% ZnO		10:1	100	270	270—312	20.6	
+0.5% TiO_2		10:1	100	294	294—329	23.6	
+2.5% TiO_2		10:1	100	314	314—341	29.4	
$CuO.Cr_2O_3$	BDH	0.5	40	300	300—410	12.2	[14]
		2.5	40	287	290—395	13.8	
		5.0	40	290	290—460	14.0	
ZnO	Merck	200:1	200			27.9	[20]
		100:1	200			29.5	
		50:1	100			31.6	
		25:1	200			27.0	
		16:1	100			28.3	
		10:1	200			27.6	
		5:1	200			29.6	
		16:1	200	224	224—242	34.0	
	3× cryst	1.0	100	247		29.5	[5]

Additive	Characteristics of AP	Amount of additive mole %, (mole ratio)	AP mg	Minimum ignition temperature °C	Temperature range °C	Activation energy kcal/mole	Ref.
CdO	Fluka	100:1	100	300	300—328	22.2	[26, 29]
	2× cryst	16:1	100	265	265—295	22.5	
		10:1	100	260			
		16:1	100	256	256—291	24.2	
MgO	Fluka	100:1	100	270.5	270.5—324	26.8	[29]
	2× cryst	50:1	100	280.0	280—324	31.8	
	3× cryst	1.0	100	330		43.5	[5]
TiO_2	BDH	2:1	100	420			[17]
$+0.1\ Cr_2O_3$	1× cryst	2:1	100	416			
$+0.5\ Cr_2O_3$		2:1	100	370			
$+1.0\ Cr_2O_3$		2:1	100	290	290—320	29.0	
$+2.5\ Cr_2O_3$		2:1	100	285	285—315	30.0	
SnO_2	BDH	2:1	100	410			[31]
	2× cryst						
$+0.01\ Cr_2O_3$		2:1	100	330	330—360	17.0	
$+0.1\ Cr_2O_3$		2:1	100	300	300—325	16.5	
$+1.0\ Cr_2O_3$		2:1	100	300	300—325	18.0	
Active carbon	2× cryst	20	16	260	260—290	40.0	[18]
$AgClO_4$	2× cryst	0.5	100	277.6	278—306	15.9	[33]
		1.0	100	277	277—306	19.2	
$Cu(ClO_4)_2$	2× cryst	1.0	100	269	269—283	22.6	[33]
$Fe(ClO_4)_3$	2× cryst	1.0	100	276	276—295	29.6	[33]
$Zn(ClO_4)_2$	Fluka	100:1	100	240	240—265	29.8	[21, 34]
	2× cryst	10:1	100	240	240—265	22.7	
$Cd(ClO_4)_2$	Fluka	100:1	100	257	257—280	31.0	[26, 34]
	2× cryst	10:1	100	260	260—285	26.0	
$Mg(ClO_4)_2$	Fluka	100:1	100	273	273—300	27.0	[34]
	2× cryst	10:1	100	270	270—300	32.0	
$LiClO_4$		69	50	290			[37]
NH_4I	2× cryst	1.0	100	248	248—281	22.5	[34]
NH_4Br	2× cryst	0.01	100	302	302—338	21.8	
		0.1	100	297	297—338	22.6	
		0.5	100	297	297—338	24.2	

be mentioned that calcium, sodium and potassium perchlorates do not exert any accelerating effect at all.

The effects of silver and copper perchlorates and of ammonium iodide on the DTA behaviour of AP were studied by FREEMAN *et al.* [43]. They showed that the above ions decrease the stability of AP. It was interesting that in their presence the

effects of γ and X-radiations also increased; *e.g.* 1 mole% silver perchlorate caused a 100-fold increase.

The thermal stability of AP is decreased significantly by the chlorate ion [44]. According to DTA studies, the effect of chlorate appears only after a crystal transformations; nevertheless the effect of even 0.001 mole% $KClO_3$ can be detected. In the presence of 0.1% $KClO_3$ the exothermic peak for the complete decomposition of AP occurred at a 150 °C temperature lower. From measurements under isothermal conditions, it turned out that chlorate ions also accelerate the decomposition of AP below 240 °C [45]. The explosion of the AP took place at 260—280 °C. Bromate and iodate ions also act similarly [45].

Interesting results were obtained by SCHMIDT [46] from the investigation of the effects of various organometallic compounds. Ferrocene and copper acetylacetonate give especially reactive compounds on interaction with the ammonium ion, and as a result of this the exothermic peak of AP at 475 °C occurs instead at 260—360 °C.

Using the DTA method under isothermal conditions at 250 °C, BOLDYREV *et al.* [47] studied the effects of various copper salts (sulphate, dichromate, benzoate, oxalate, lactate and nitrate) on the thermal decomposition of AP. They showed that the effectiveness of the additives depended on the course of their thermal decomposition. Salts which are stable at the temperature of the decomposition of AP did not exert a catalytic effect (sulphate and dichromate). An acceleration effect was found, however, in the presence of benzoate, the decomposition of which occurred parallel with that of the AP. Even greater effects were observed in the case of other salts. In the evaluation of the results it was assumed that the decomposition of AP is affected not only by the oxides formed in the decomposition of the salts but also by the gases which also evolved.

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КИНЕТИКА КАТАЛИТИЧЕСКОГО РАЗЛОЖЕНИЯ ПЕРХЛОРАТА АММОНИЯ

Ф. Шоймоши

В работе автор подытоживает важнейшие результаты, достигнутые в области кинетического изучения распада перхлората аммония, катализированного разными окислами металлов и солями. Автор рассматривает влияние добавок на взрыв перхлората аммония и устанавливает те свойства солей металлов, которые играют основную роль в катализе распада перхлората аммония.